A Polymer Equation of State[1]

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ABSTRACT

An equation of state is proposed to consider the rotational contribution of hard dumbbell molecules on the compressibility of fluids. Then, using this equation and based on perturbation theory, an equation of state is developed to describe the PVT behavior of polymer melts. The developed equation is in a segmental form, *i.e.*, it needs the segmental parameters of a polymer for the calculation of PVT properties. This polymer equation of state is fourth order in volume and needs 3 characteristic parameters for each segment of a polymer, namely, the external degrees of freedom of rotation, segmental characteristic volume and segmental characteristic temperature. When the polymer equation of state was used to fit the PVT of polymer melts for a wide range of temperature and pressure, it was obtained that the calculated molar volume is generally within 0.1% of the experimental data. The ability of the polymer equation of state is also compared with other equations of state for polymers.

KEY WORD: dumbbell molecule; equation of state; liquid; PVT; polymer melts, rotational compressibility factor

1. INTRODUCTION

The PVT of polymer melts are important to chemical engineers. Equations of state that describe this PVT behavior are equally important. However, the ability of equations of state to predict the PVT of polymer melts is different especially at very low and very high pressures. Rodger [1] reviewed the equations of state for calculating the PVT of polymer melts.

Beret and Prausnitz [2] developed the perturbed hard-chain theory (PHCT) equation of state based on Prigogine's hypothesis [3], *i.e.*, at high densities, all density dependent degrees of freedom can be treated as equivalent translational degrees of freedom. This equation of state covers a wide variety of molecules from simple molecules like argon to complex molecules like polymers. Kim et al. [4] simplified the PHCT equation of state (SPHCT) using the lattice theory for the attraction contribution of molecular segments. Tochigi et al. [5] introduced a simple cubic equation of state based on the Prigogine's hypothesis [3] for the calculation of the PVT of liquid polymers. Sy-Siong-Kiao et al. [6] obtained an equation of state for liquid polymers by simplifying the molecular form of the chain of rotator group contribution (CORGC) equation of state [7,8,9]. The simplifying assumption was that as a molecule grows larger, the rotational mode of molecular motion becomes dominant but the translational mode remains constant and independent of the size of the molecule.

Although the above equations of state satisfy the ideal gas state limit, they have deficiency at close-packed limit, *i.e.*, they fail to satisfy the condition that $Z \to \infty$ when $v^*/v \to 1$. The latter condition is important at high pressures. Furthermore, for most of the

equations of state for liquid polymers, the predictions get worse at low pressures. Therefore developing an equation of state to satisfy the above condition and is still accurate enough at low and high pressure is justified.

In this work, firstly, an equation is proposed to consider the rotational contribution of hard dumbbell molecules on the compressibility factor of fluids. Then based on this equation and Sy-Siong-Kiao et al. [6] assumption, a simple and accurate equation of state for the whole liquid polymers region is obtained. This equation of state should satisfy the ideal gas and close-packed limits.

2. MODEL

2.1. Rotational Compressibility Factor for Hard Dumbbell Molecules

The compressibility factor for hard dumbbell molecules is made up of two contributions: The contribution from translational motion and the one from rotational motion. For translational compressibility factor, the equation from Khoshkbarchi and Vera [10] is used:

$$Z_{tran} = \frac{1 - 1/25\zeta - 2/5\zeta^2 - 5/4\zeta^3 + 9/50\zeta^5 + 71/50\zeta^{12}}{(1-\zeta)^3} \tag{1}$$

where Z_{tran} is compressibility factor for the translational mode of motion of molecules, ζ is reduced density (v^*/v), and v^* is close-packed molar volume. For the rotational compressibility factor, the following equation is proposed:

$$Z_{db,rot} = \frac{a_1\zeta + a_2(\alpha + 1)\zeta^2 + a_3(\alpha + 1)\zeta^3}{(1-\zeta)^2} \tag{2}$$

with $a_1=2$, $a_2=3$, and $a_3=-4$. The parameter α is expressed by:

$$\alpha = \frac{(1+L)(2+L)}{(2+3L-L^3)} \tag{3}$$

where $L=l/\sigma$ is the ratio of the spheres (center to center) distance to the diameter. Both Eqs.(1) and (2) satisfy the close-packed limit, i.e., $Z\rightarrow\infty$ as $\zeta\rightarrow1$. The constant a_1, a_2 and a_3 in Eq. (2) were obtained by matching the pseudo experimental data (Monte Carlo simulation) [11] with the following equation for hard-dumbbell molecules

$$Z_{db} = Z_{tran} + Z_{db,rot} \tag{4}$$

where Z_{tran} is calculated from Eq.(1) and $Z_{db,rot}$ from Eq.(2). Table 1 compares the results of Eq.(4) with Monte Carlo simulation data and the results of other models. Explainations will come in the following sections. Using Eq.(2), an equation of state will be obtained in the following section.

2.2 The Polymer Equation of State

The repulsive forces predominantly determine the structure of a liquid polymer and the attractive forces contribute as a perturbation. Moreover, as a molecule grows larger the rotational contribution of repulsive forces become dominant while the translational contribution remains constant, So a configurational partition function can be factored as [6,12]:

$$Q_{conf} = q_{db,rot}^{Nc/2} Q_{attr} \tag{5}$$

where $q_{db,r}$ is the rotational partition function for a dumbbell molecule with 2 rotational degrees of freedom, c is the rotational degrees of freedom for a segment in a polymer molecule, N is the total number of segments in all of the polymer molecules and Q_{attr} is the perturbation attraction partition function between all of the segments in the polymer molecules.

The attraction partition function, Q_{attr}, is expressed by [4]:

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$$Q_{attr} = e^{-Z_M(c/3+1)\ln\left(\frac{v}{v+v^*Y}\right)}$$
(6)

where (c/3+1) was substituted for C (one third of the total number of external degrees of freedom) in the original equation. The parameter Z_M has a value of 36 and represents the maximum coordination number, v^* is the characteristic volume for a segment in a polymer molecule and Y is defined by:

$$Y = \exp\left(\frac{T^*}{2T}\right) - 1$$
(7)

where T^* is the characteristic temperature of the segment in the polymer molecule.

Upon differentiation of Eq.(1) according to [13]:

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$
(8)

where p is pressure, T is temperature and k is Boltzman constant and using Eq.(5) and the compressibility factor relation ($Z=PV/NkT$), we arrive at:

$$Z = \frac{c}{2}Z_{db,rot} - \frac{Z_M(c/3+1)v^*Y}{v+v*Y}$$
(9)

When Eq.(2) is used for $Z_{db,rot}$, the resulting polymer equation of state will be

$$Z = \frac{c}{2}(\alpha-1)\frac{2\zeta + 3(\alpha+1)\zeta^2 - 4(\alpha+1)\zeta^3}{(1-\zeta)^2} - \frac{Z_M(c/3+1)v^*Y}{v+v^*Y}$$
(10)

where v is the segmental molar volume (V/s), s is the number of segments in a polymer molecule, and Z ($=Pv/RT$) is the segmental compressibility factor. To describe the PVT of liquid polymers using Eq.(10), 3 characteristic parameters c, v^*, and T^* are required for a segment of a polymer molecule. For 10 polymers, the characteristic parameters are given in Table 2. In the calculations, the parameter α (dumbbell constant) is taken 1.078 for all polymer segments. This is the value that was calculated by chien et al. [12] for ethane molecule as a reference dumbbell molecule.

3. RESULTS AND DISCUSSION

Table 1 compares the compressibility factor of hard dumbbell molecules calculated from Eq.(4), Hard Convex Body (HCB) [11] and a (2,2) Pade' approximant equation with pseudo experimental data [11]. The comparisons are for $L=0.6$ and $L=1$. As can be seen, both this work and HCB agree well with the pseudo experimental data and this work is a little better. For $L=0.6$, the predicted second and third virial coefficients (B/v_d, and C/v_d^2, where v_d is dumbbell volume) are 4.431 and 13.066, respectively. These values agree with the exact values 4.474 and 12.112. For $L=1$, the predicted second and third virial coefficients are 5.348 and 20.480. The exact values are 5.444 and 16.928, respectively.

Table 2 gives the characteristic parameters of 10 polymer segments. Notice that these values are for the repeating units of each polymer. For each polymer segment in a polymer molecule, these parameters were optimized using a nonlinear regression package [14] and the following objective function:

$$\Delta = \sum_i^{np} \frac{\left| v_i^{cal} - v_i^{exp} \right|}{v_i^{exp}} \tag{11}$$

where np is the number of points used for fitting, and the superscripts *cal* and *exp* stand for calculated and experimental values, respectively. The averages of absolute percent error for the calculation of the molar volume are given in Table 3. Table 3 also compares the abilities of 3 other equations of state for the same calculations. They were obtained using the same experimental data and the same procedure as we did for our polymer equation. As can be seen our equation is a little better than the SPHCT and TKM equations of state but worse than Sy-Siong-Kiao et al. [6]. The remarkable superiority for the Sy-Siong-Kiao et

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al. [6] equation comes from the fact that the Sy-Siong-Kiao et al. [6] equation has 4 adjustable parameters while the three others have 3 adjustable parameters.

Figs. 1 and 2 illustrate the calculated liquid volume percent deviation (LVPD) of polyisobutylene and polystyrene using our equation of state as a function of pressure and temperature, respectively. The LVPD is defined by:

$$LVPD = \frac{v^{cal} - v^{\exp}}{v^{\exp}}(100) \qquad (12)$$

Fig. 1 indicates that irrespective of temperature and with increasing pressure, the deviation of calculated liquid volumes increases from the experimental values. At temperatures less than 429 K, the polymer equation of state under-predicts the experimental values and at temperatures higher than 429 K it upper-predicts the experimental liquid volumes.

The conclusion that can be drawn from Fig. 2 is that at each isobar, the liquid volume percent deviation is not changed appreciably with increasing pressure.

4. **CONCLUSION**

A model to represent the compressibility of hard dumbbell molecules has been proposed. Based on the rotational part of this model and perturbation theory a polymer equation of state has been developed. This equation is fourth order in volume and requires 3 characteristic parameters for the repeating unit of each polymer in order to describe the PVT of the liquid polymers. The *%AAD* is generally within 0.1% of experimental data.

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Table 1
Calculated values of compressibility factor from different models.

L=0.6					L=1				
y	Exact[11]	This work	HCB[a]	PA[b]	y	Exact[11]	This work	HCB	PA
0.1047	1.64	1.64	1.63	1.63	0.1047	1.83	1.83	1.80	1.80
0.2094	2.84	2.79	2.77	2.82	0.2094	3.38	3.43	3.33	3.35
0.3142	5.02	4.94	4.89	5.36	0.3142	6.37(6.45)	6.45	6.31	6.42
0.4189	9.24	9.15	9.15	13.22	0.3665	8.84	8.88	8.82	9.07
					0.4189	12.4	12.31	12.50	13.01
					04712	17.5	17.27	18.02	19.7
					0.4974	20.7	20.60	21.83	

[a] Hard Convex Body, [b] Pade' Approximant

Table 2
List of polymers, the range of temperature and pressure and the characteristic parameters of the new equation of state

Polymer	T. Range (K)	P.Range (MPa)	Source	c	v^* (cm^{3}mol^{-1})	T^* (K)
Polymethylene (PM)	415-472	0.1-200	[15]	4.6193	25.1116	43.087
Polystyreme (PS)	388-468	0.1-200	[16]	7.1783	82.6291	78.523
Poly(o-methylstyrene) (PoMS)	412-470	0.1-180	[16]	9.0728	95.0159	83.651
Phenoxy (PH)	341-573	0.1-176.6	[17]	34.1285	196.9218	88.017
Polyisobutylene (PIB)	326-383	0.1-100	[1]	4.4616	51.1901	62.636
Poly(methyl methacrylate) (PMMA)	387-432	0.1-200	[1]	8.8536	68.7372	76.380
Polysulfone (PSF)	528-644	0.1-196	[18]	49.3583	279.4974	93.084
Poly(tetrafluoroethylene) (PTFE)	603-645	0.1-39	[19]	19.7815	24.2408	28.018
Poly(vinyl acetate) (PVAc)	308-373	0.1-80	[1]	10.3671	57.2208	61.521
Poly(vinyl chloride) (PVC)	373-423	0.1-200	[1]	3.9131	37.3470	61.275

Table 3
Ability of different equations of state (*%AAD*[a]) for the calculation of the molar volume of polymer melts.

Polymer	np	This work [b]	SPHCT[c]	TKM[d]	PCOR[e]
Polymethylene (PM)	67	0.052	0.073	0.140	0.048
Polystyreme (PS)	69	0.079	0.072	0.100	0.058
Poly(*o*-methylstyrene) (PoMS)	50	0.038	0.061	0.049	0.035
Phenoxy (PH)	42	0.169	0.267	0.110	0.053
Polyisobutylene (PIB)	42	0.039	0.055	0.060	0.032
Poly(methyl methacrylate) (PMMA)	60	0.060	0.055	0.080	0.041
Polysulfone (PSF)	53	0.093	0.130	0.088	0.083
Poly(tetrafluoroethylene) (PTFE)	21	0.216	0.136	0.105	0.108
Poly(vinyl acetate) (PVAc)	63	0.011	0.032	0.019	0.008
Poly(vinyl chloride) (PVC)	87	0.065	0.066	0.089	0.006
Average		0.070	0.085	0.084	0.041

[a] $\% AAD = (100/np) \sum_{i}^{np} \left| v_{i,cal} - v_{i,\exp} \right| / v_{i,\exp}$, [b] Using the characteristic parameters given in Table 1, [c] Kim et al. [4], [d] Tochigi et al. [5], [e] Sy-Siong-Kiao et al. [6]

Figure Captions

Fig. 1. Liquid volume percent deviation of polystyrene (PS) as a function of pressure with temperature as a second parameter.

Fig. 2. Liquid volume percent deviation of polyisobutylene (PIB) as a function of temperature with pressure as a second parameter.
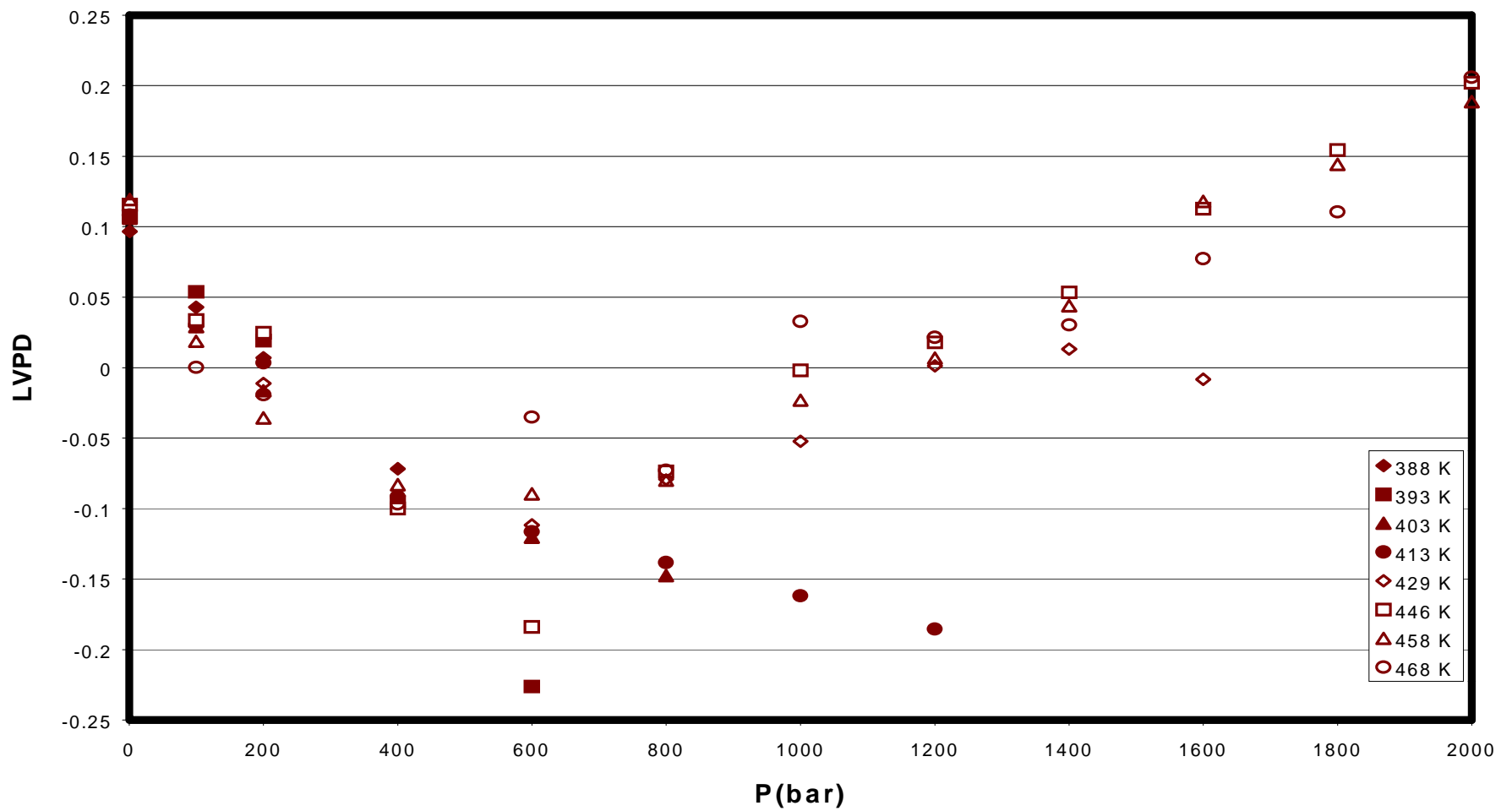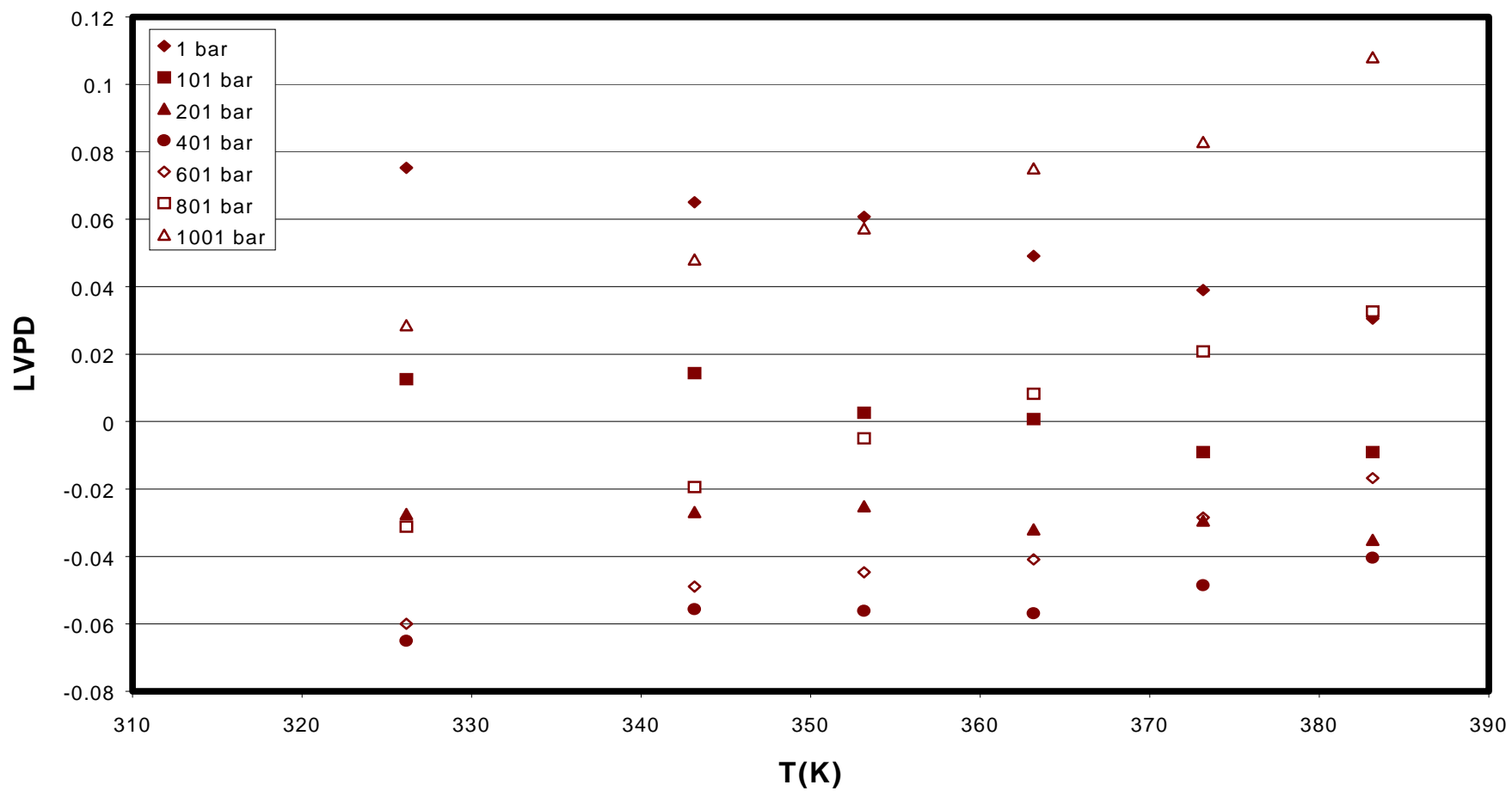
Fig. 1.

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Fig. 2.

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